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㉖ The removal of phenols from phenol-containing streams.

㉗ Phenols are removed from phenol containing streams as
the corresponding metal phenate. The metal phenate is con-
tacted with steam at 250°C to 450°C thereby producing
phenols and metal hydroxides.

EP 0 112 723 A2

THE REMOVAL OF PHENOLS FROM PHENOL-
CONTAINING STREAMS

1

2 The present invention relates to the production
3 of phenols from phenol-containing streams

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9 The presence of phenols in various hydrocar-
10 bonaceous streams is troublesome. For example, the
11 presence of phenols in liquids produced from coal causes
12 instability of these liquids over a period of time by
13 increasing the viscosity, the color intensity, and
14 causing the separation of resinous materials. Moreover,
15 without extensive hydrotreatment, coal liquids are
16 generally not compatible with petroleum liquids of
17 comparable boiling point. Thus, solids separation
18 caused largely by high concentrations of phenols, leads
19 to severe operability problems for coal/petroleum liquid
20 blends. Furthermore, hydrodesulfurization and hydro-
21 denitrogenation of coal liquids are required prior to
22 reforming into motor gasoline. These steps would
23 require a relatively large consumption of hydrogen for
24 the phenol-rich coal liquids because of the extensive
25 deoxygenation of phenols to water.

26 Various methods for removing these troublesome
27 phenols from hydrocarbonaceous streams are taught in
28 the art. For example, it is taught in U.K. Patent No.

1 494,450 that weakly acid-reacting organic substances
2 such as phenols, can be separated from hydrocarbonaceous
3 streams by use of alkali metal or alkaline-earth metal
4 oxides or hydroxides in the presence of an auxiliary
5 agent such as an aliphatic polar compound. It is taught
6 in U.S. Patent No. 4,256,568,

7 that phenols react with these
8 oxides and hydroxides resulting in the formation of
9 metal phenates, which are easily separated from the
10 purified stream. Further, it is taught in Ges. Abhandl.
11 Kenninis Kohle, Vol. 4, pp. 237-63 (1919), that certain
12 metal phenates, such as calcium phenoxide, can be heated
13 in the presence of carbon dioxide to yield phenols and
14 calcium carbonate.

15 Still another method for separating such
16 phenols is taught in U.S. Patent No. 4,256,568, which
17 method comprises treating a phenol-containing stream,
18 such as a coal liquid, with a multivalent metal oxide
19 and/or hydroxide. The resulting hydroxy metal phenate
20 is then pyrolysed to a temperature of about 650°C to
21 recover the phenols and an oxide of the multivalent
22 metal.

23 Another method is disclosed in U.S. Patent No.
24 4,299,691 which also employs a multivalent metal oxide
25 and/or hydroxide for removal of phenols from phenol-
26 containing hydrocarbonaceous streams. The resulting
27 hydroxy metal phenates are then reacted with one
28 or more C₁ to C₁₀ aliphatic alcohols or C₇ to C₁₆ aryl-
29 alkyl primary alcohols.

30 Although some of these methods are commer-
31 cially feasible in various industries, there is still
32 a need to develop a process for removing, from hydro-
33 carbonaceous streams, troublesome phenols and recovering

1 the phenols and a metal hydroxide in a more efficient
2 and inexpensive way.

3

4 In accordance with the present invention,
5 phenols are removed from phenol-containing streams and
6 the phenols are regenerated by a process which com-
7 prises: a) contacting the stream with one or more metal
8 oxides or hydroxides which are capable of forming a
9 metal phenate with the phenols of the stream, wherein
10 the stream is contacted at a temperature below the
11 decomposition temperature of the resulting metal phenate
12 or the temperature at which detrimental thermal degrada-
13 tion of the stream occurs; b) separating the resulting
14 metal phenate from the stream; and c) treating the metal
15 phenate with steam at a temperature from about 250°C to
16 about 450°C thereby forming phenols and hydroxides of
17 the metal of the phenate.

18 In preferred embodiments of the present
19 invention, the stream is a phenol-containing hydrocar-
20 bonaceous stream, and the metal composition is an alkali
21 metal hydroxide employed in a sufficient concentration
22 so that at least 15% of the total phenols present are
23 removed from the stream.

24 In other preferred embodiments of the present
25 invention the phenol-containing hydrocarbonaceous stream
26 is a coal liquid and the metal is selected from
27 sodium and potassium and the result-
28 ing metal phenate is contacted with steam at a temper-
29 ature of about 300°C to 350°C.

1 In the drawings:

2 Figure 1 is a plot of the amount of phenols
3 recovered from calcium hydroxy phenate at various
4 temperatures for a given period of time and at a molar
5 ratio of water to calcium hydroxy phenate of 12 to 1; and

6 Figure 2 illustrates that at a given tempera-
7 ture such as about 350°C and in a given period of time,
8 various amounts of phenol can be recovered from calcium
9 hydroxy phenate by adjusting the molar ratio of water to
10 calcium hydroxy phenate.

11

12 Phenol-containing hydrocarbonaceous streams
13 which can be treated according to the present invention
14 include, but are not limited to, those streams resulting
15 from the processing of coal, petroleum, and those
16 existing as impurities in such parent streams as linear
17 paraffins.

18 The term phenol-containing hydrocarbonaceous
19 stream means a hydrocarbonaceous stream containing
20 measurable amounts of phenol compounds in which one or
21 more hydroxyl groups are attached to an aromatic ring
22 and where the aromatic ring may also contain a hetero-
23 atom (e.g. nitrogen in a pyridine ring). Non-limiting
24 examples of such phenol compounds include phenol itself,
25 the cresols, xylenols, recorcinol, naphthols, 8-hydroxy-
26 quinoline and 4-hydroxyquinoline. The phenol-containing
27 hydrocarbonaceous stream, exclusive of the phenol
28 compounds, also contains at least 25 wt.% of compounds
29 containing carbon and hydrogen, though other atoms (e.g.
30 nitrogen, oxygen, sulfur) may also be present.

1 The stream must also contain a sufficient
2 amount of water so that metal phenates will form when
3 the stream is contacted with the metal oxide or hy-
4 droxide composition. The term, sufficient amount of
5 water, as used herein, means at least that amount of
6 water which would allow the formation of metal phenates
7 within two hours from the time the stream is contacted.
8 If the stream is substantially dry, or free of water, at
9 least a sufficient amount of water must be added.

10 The present invention is not dependent on any
11 particular method of producing the phenol-containing
12 stream. For example, if the stream is a hydrocarbon-
13 aceous stream any coal liquid which contains phenols can
14 be treated regardless of the way it was produced. Non-
15 limiting examples of types of processes for producing
16 coal liquids include pyrolysis, solvent refining, direct
17 hydrogenation with or without a catalyst, catalytic or
18 noncatalytic hydrogenation in the presence of a non-
19 hydrogen donor solvent and catalytic or non-catalytic
20 liquefaction by a hydrogen donor solvent method.
21 Furthermore, waste water streams which contain phenols
22 may also be treated in accordance with the present
23 invention .

24 Although not wishing to be limited hereby, one
25 preferred method for obtaining coal-liquids is the Exxon
26 Donor Solvent (EDS) process for the liquefaction of coal
27 which is described in U.S. Patent No. 3,617,513 and
28 incorporated herein by reference. Briefly stated, the
29 EDS process involves the formation of a slurry of coal
30 in a hydrogen-donor solvent, such as tetralin, and
31 maintained at elevated temperatures of about 260°C
32 to 370°C under agitation. Holding the coal at these

1 temperatures causes the coal to disintegrate and dis-
2 solve without the breaking of a significant number of
3 coal covalent bonds, thereby ensuring only a limited
4 amount of free radical formation. The slurry is
5 held at these temperatures, under agitation, until the
6 convertible portions of the coal are substantially
7 uniformly dispersed in the hydrogen-donor solvent. When a
8 suitable dispersion is indicated, for example, by
9 viscosity measurements conducted on the slurry, the
10 temperature of the slurry is increased to bond-breaking,
11 or depolymerization, temperatures, generally above about
12 370°C. Pressures effective to maintain the dispersant
13 slurry substantially in the liquid phase, generally
14 about 350 p.s.i.g. to 3500 p.s.i.g. are employed. In
15 this second temperature stage, the dissolved coal
16 particles are well dispersed in the hydrogen-donor
17 solvent and the chance of a hydrogen-donor stabilization
18 of free radicals generated by bond-breaking is maximised.
19 At the same time, the chance for free radicals to
20 combine with one another to produce undesirable mole-
21 cules is minimised. The dispersed slurry is maintained
22 at elevated temperatures, above about 370°C, until a
23 predetermined conversion of the coal is obtained. The
24 liquid product, which contains phenols, is then dis-
25 tilled, hydrogenated, the gases drawn off, and the
26 bottoms removed for coking and gasification.

27 In accordance with the present invention,
28 the phenol-containing stream is treated with one or
29 more oxides and/or hydroxides of metals capable of
30 forming a metal phenate with the phenols of the stream.
31 Oxides and hydroxides of both monovalent metals, prefer-
32 ably the alkali metals, sodium and potassium; and
33 multivalent metals, such as the alkaline-earth metals,

1 are suitable for use herein: as long as they are
2 capable of forming metal phenates with the phenols of
3 the treated stream. The choice of the one or more metal
4 oxides or hydroxides employed herein is dependent on
5 such factors as the desired final level of phenols-
6 content of the stream, the reactivity of the particular
7 phenol compounds to the metal, and the type of phenol
8 one wishes to separate. For example, multivalent metal
9 oxides and hydroxides are more reactive with the less
10 sterically hindered phenols and therefore can be used to
11 selectively remove such phenols, leaving most of the
12 more sterically hindered phenols in the stream. On the
13 other hand, oxides and hydroxides of monovalent metals,
14 such as the alkali metals, will remove phenols without
15 preference to steric factors. Consequently, if a stream
16 contains both sterically hindered and non-hindered
17 phenols, and if it is predetermined to remove substan-
18 tially all of the phenols regardless of steric hindr-
19 ance, then an oxide and/or hydroxide of an alkali metal
20 would be employed. For purposes herein, the term, metal
21 phenate, also includes hydroxy metal phenates which
22 result from the reaction of certain multivalent metal
23 oxides and hydroxides with phenols of the stream.

24 In the practice of the present invention, the
25 stream is contacted at a certain temperature.

26 This
27 is generally from about room temperature (20°C) to
28 either the decomposition temperature of the resulting
29 metal phenate or the temperature at which detrimental
30 thermal degradation of the stream occurs, whichever
31 temperature is lower. For example, when calcium is
32 the metal of the oxide or hydroxide used herein, the
33 decomposition temperature of its resulting hydroxy

1 calcium phenate is about 450°C. Detrimental degra-
2 dation of the stream, as used herein means that when the
3 stream reaches a certain elevated temperature, degrada-
4 tion reactions, such as polymerization leading to an
5 increase in high boiling fractions, cracking leading to
6 low value gaseous products, and coke formation leading
7 to fouling, occur to such a degree that the overall
8 chemical properties of the stream are adversely affected.
9 The decomposition temperature of any resulting metal
10 phenate, as well as the temperature at which detrimental
11 thermal degradation of the stream occurs, can be easily
12 determined by one having ordinary skill in the art and
13 further elaboration is therefore not necessary.

14 The amount of metal composition needed in the
15 practice of the present invention is dependent on the
16 amount of metal required to react with a predetermined
17 amount of the phenols of the stream. Although it may be
18 desirable to remove as much of the phenols from the
19 stream as possible, one may wish to remove only a
20 certain minimum amount based on economic considerations.

21 The concentration of phenols in the hydro-
22 carbonaceous stream can be determined by conventional
23 analytical methods such as non-aqueous titration. Th
24 amount of multivalent metal needed to remove a predeter-
25 mined amount of phenols can be expressed as the mol
26 ratio of metal (as the oxide and/or hydroxide) to
27 phenolic-oxygen (in the feed stream). The preferred mol
28 ratio of metal to phenolic-oxygen needed herein is that
29 ratio which, when the metal oxides and/or hydroxides are
30 contacted with the stream, will ensure the removal of at
31 least about 15 wt.% of the phenols from the feed stream
32 at a temperature of about 25°C for a contact time of
33 about 90 minutes. The wt.% of phenol removal is based
34 on the total weight of phenols in the stream.

1 It will be noted that because the activity of
2 some metals is greater than that of other metals under a
3 given set of conditions, less of the more active metal,
4 for a given amount of phenols in the feed stream, will
5 be required to remove a predetermined amount of the
6 phenols from the stream. For example, at a temperature
7 of 25°C and a contact time of 90 minutes, about 17 wt.%
8 of phenols are removed from a phenol-containing coal
9 liquid using zinc hydroxide at a metal to oxygen mol
10 ratio of 1.0; whereas, at the same temperature and
11 metal to oxygen mol ratio, about 72 wt.% of phenols are
12 removed from the same coal liquid when calcium hydroxide
13 is used. The relative activity of one metal to another
14 is known in the art and the ratio of any given metal to
15 oxygen can be determined by either routine experimenta-
16 tion or calculation by one having ordinary skill in the
17 art.

18 In order to achieve a high percentage of
19 phenol removal with any metal oxide or hydroxide, a
20 multistage process can be used. For example, at a
21 calcium to oxygen mol ratio of 0.2, a contact time of 90
22 minutes, and at a temperature of 25°C, 48 wt.% removal
23 of phenols from a coal liquid is achieved. If the
24 treated coal liquid is contacted a second time at the
25 same mol ratio, time, and temperature conditions as the
26 first stage, an overall 77 wt.% removal of phenols is
27 achieved. Therefore, it may be desirable to contact the
28 liquid effluent from a previous stage many times over to
29 effect substantially total removal of the phenols from
30 the stream. For example, after initial contact of the
31 stream with the metal composition, the treated stream is
32 separated from the resulting metal phenate and passed
33 along to another stage for contact with additional metal
34 composition. This sequence can be repeated as often as
35 practical and desirable.

1 It may be desirable from an energy savings
2 point of view that the phenol-containing hydrocarbon-
3 aceous stream be at elevated temperatures when contacted
4 with the metal composition. In this context, elevated
5 temperatures means temperatures greater than room
6 temperature but lower than the decomposition temperature
7 of the resulting metal phenate. Generally, the phenol-
8 containing feed stream will result from a chemical,
9 petroleum, or coal process and will leave such process
10 at elevated temperatures whereupon it can be treated
11 directly with the metal composition as long as the
12 temperature of the stream is lower than the decomposi-
13 tion temperature of the resulting metal phenate.
14 Therefore, the temperature of the phenol-containing feed
15 stream may be dependent on the source and process for
16 its production and may have to be cooled to a lower
17 temperature before treatment.

1

2

3 Upon contacting the hydroxy metal phenate with
4 steam, the phenol compound is regenerated and a hydrox-
5 ide of the multivalent metal is produced. This hydrox-
6 ide can be recycled in a continuous process. For
7 purposes of the present invention, the terms water and
8 steam are sometimes used interchangeably.

23 It will be noted that, if present, carboxylic
24 compositions may also be removed from the hydrocarbon-
25 aceous stream when treated according to the present
26 invention.

27 One preferred method of the present invention
28 for removing phenols from a stream is a continuous
29 stirred tank reactor process which comprises contacting
30 a phenol-containing hydrocarbonaceous feed stream with a
31 predetermined concentration of a composition comprised
32 of a metal oxide, metal hydroxide, or both, which metal
33 compositions are capable of forming metal phenates with

1 the phenols of the streams. This metal composition can
2 contact the hydrocarbonaceous stream as either a solid
3 or as an aqueous slurry containing the solid metal
4 composition, if the metal is a multivalent metal. It is
5 preferred that the hydrocarbonaceous stream be contacted
6 with only solid particles of the multivalent metal
7 composition so as to eliminate an aqueous phase.

8 Another preferred method for removing phenols
9 is the use of a continuous extraction column with a
10 liquid separator.

11 As previously discussed, the amount of metal
12 composition contacting the stream is dependent on, among
13 other things, the desired mol ratio of metal to phenolic-
14 oxygen in the stream. For purposes of this invention,
15 it is preferred that the mol ratio be at least that
16 which will remove at least 15 wt.% of phenols from the
17 stream. The metal composition and stream are thoroughly
18 mixed to ensure contact of the phenols with the metal
19 composition. The phenols in the stream react with the
20 metal composition, thereby forming a metal phenate. The
21 metal phenate is separated from the stream by any con-
22 ventional method and the hydrocarbonaceous effluent
23 portion of the stream is passed along for further
24 processing, further contacting with additional multi-
25 valent metal compositions, or such treatment as hydro-
26 fining. The metal phenate is removed and dried and
27 any residual portions still containing phenolic func-
28 tionality can be recycled to the feed stream. The dried
29 metal phenate is treated with steam at a temperatur
30 from about 250°C to 450°C, preferably from about 350°C
31 to 450°C for an effective amount of time, thereby gen-
32 erating phenols as well as metal hydroxides. The
33 phenols are collected and the metal hydroxides are
34 recycled to the hydrocarbonaceous feed stream. Of

1 course, multistage processing can be performed until the
2 desired level of phenol removal is achieved.

3 Other methods which can be used in practising
4 the present invention for removing phenols from a
5 hydrocarbonaceous stream, are fluidized or fixed bed
6 processes using phenol sorbent materials. - Suitable
7 phenol sorbent materials include basic ceramic sorbents
8 such as barium titanate, calcium titanate, calcium
9 aluminate cement, and the like.

10 Other conventional solid/fluid processes can
11 also be used. Non-limiting examples of such other
12 processes include cyclic fluid bed, tube flow reactor,
13 and moving bed processes.

14 The presence of the metal phenate, which is
15 formed during the practice of the present invention is
16 supported by conventional elemental analysis. That is,
17 the amount of carbon, hydrogen and metal for each metal
18 phenate can be calculated empirically, then substan-
19 tiated by elemental analysis.

20 The following examples serve to more fully
21 describe the present invention. It is understood that
22 these examples in no way serve to limit the true scope
23 of this invention, but rather, are presented for illus-
24 trative purposes.

25 Examples 1-4

26 Various multivalent metal oxides were used to
27 extract phenols from a phenol-containing naphtha cut
28 derived from a coal liquefaction process and containing
29 a sufficient amount of water. The naphtha cut contained

1 1 mmol of oxygen/gm of naphtha, which oxygen is essen-
 2 tially all present as phenols. Concentrations of oxides
 3 were used to give a mol ratio of metal in the oxide to
 4 phenolic oxygen in the naphtha cut of 1.0. The naphtha
 5 cut in each instance was contacted for 90 minutes with
 6 the multivalent metal oxide at a temperature of 25°C.
 7 A hydroxy metal phenate resulted and was separated from
 8 the treated naphtha cut. The amount of phenols removed
 9 was determined by gas chromatography wherein the phenol
 10 content of the non-treated naphtha was compared to that
 11 of the treated naphtha. The results are set forth in
 12 Table I below:

13 TABLE I

14 Effect of Metal Atom on Removal of Phenols
 15 When Used in Oxide Form

16 <u>Ex.</u>	<u>Metal Ion</u>	<u>Wt.% of Phenol Removal</u>
17 1	Ca ⁺⁺	49
18 2	Sr ⁺⁺	65
19 3	Ba ⁺⁺	100
20 4	Ni ⁺⁺⁺	25

21 The above table shows that at a mol ratio
 22 of metal to phenolic-oxygen of 1, at a temperature of
 23 25°C and for a contact time of 90 minutes, the oxides
 24 of Ca, Sr, Ba and Ni³⁺ are able to remove at least
 25 25 wt.% of the phenols from the phenol-containing
 26 naphtha stream. The weight percent of phenol removed is
 27 based on the total weight of phenols in the untreated
 28 naphtha stream.

29 Comparative Examples A-D

30 For comparative purposes, various multivalent
 31 metal oxides, other than those of Examples 1-4, were

1 used according to the conditions set forth in Examples
2 1-4. The results are shown in Table II below:

3 TABLE II

4 Effect of Metal Atom on Removal of Phenol
5 When Used in Oxide Form

6	<u>Ex.</u>	<u>Metal Ion</u>	<u>Wt.% of Phenol Removal</u>
7	A	Mg ⁺⁺	5
8	B	Zn ⁺⁺	9.8
9	C	Ni ⁺⁺	9
10	D	Ce ⁴⁺	3

11 The above table shows that not all multivalent
12 metal oxides are capable of removing at least 15 wt.% of
13 phenols from the untreated naphtha cut.

14 Examples 5-10

15 Various multivalent metal oxides were used to
16 remove phenols from the same naphtha cut and under the
17 same conditions set forth in Examples 1-4 except, a
18 stoichiometric amount of water was added to completely
19 (hydrate) convert the metal oxide to the corresponding
20 hydroxide. The results are set forth in Table III
21 below.

1

TABLE III

2
3

Effect of Metal Atom on Removal of Phenols
When Used in Hydroxide Form

4	<u>Ex.</u>	<u>Metal Ion</u>	<u>Wt.% of Phenol Removal</u>
5	5	Ca ⁺⁺	72
6	6	Sr ⁺⁺	99
7	7	Ba ⁺⁺	100
8	8	Zn ⁺⁺	17
9	9	Ni ⁺⁺	15
10	10	Ni ⁺⁺⁺	53

11 Table III shows, that generally, the multi-
12 valent metal hydroxide is preferred over the correspond-
13 ing oxide because of its increased phenol removal
14 capabilities. Although when barium is the multivalent
15 metal, substantially all of the phenols are removed with
16 either the oxide or hydroxide form.

17 Comparative Example E

18 Comparative example D was repeated except a
19 stoichiometric amount of water was added to completely
20 (hydrate) convert cerium oxide to cerium hydroxide during
21 phenol removal. After analysis by gas chromatography,
22 it was found that the amount of phenol removal for cerium
23 hydroxide was 7 wt.% vs. 3 wt.% for the corresponding
24 oxide. This shows that even the hydroxide form of some
25 multivalent metals is incapable of removing at least
26 15 wt.% of the phenols from a phenol-containing naphtha
27 stream.

1 Examples 11-18

2 Various mol ratios of calcium, in its hydrox-
3 ide form, to oxygen, in the naphtha cut, were used to
4 remove phenols from the naphtha stream of Examples 1-4.
5 These runs were performed at 25°C for a 90 minute
6 contact time in either 1 or 2 stage processes as indi-
7 cated below. That is, if the process was a two stage
8 process, the naphtha stream (treated or untreated
9 depending on the stage) was contacted with calcium
10 hydroxide for 90 minutes in each stage. The results are
11 set forth in Table IV below.

12 TABLE IV

13 Comparison of Removal Efficiencies for 1 and
14 2 Stage Batch Processes at Various M/O Values

15				Wt.% of
16	<u>Ex.</u>	<u>M/O Ratio</u>	<u>No of Stages</u>	<u>Phenol Removal(a)</u>
17	11	0.1	1	32
18	12	0.1	2	54
19	13	0.2	1	48
20	14	0.2	2	77
21	15	0.4	1	61
22	16	0.4	2	81
23	17	0.8	1	70
24	18	0.8	2	-

25 This table shows the advantage of using more
26 than one stage for removal of phenols from a phenol-
27 containing naphtha stream. For example, a two stage
28 process using a specific M/O value for each stage is
29 capable of removing more of the phenols than a one stage
30 process using an M/O value double that of the corre-
31 sponding two stage process under the same conditions.

1 Each of the following examples was carried
2 out by use of a small fixed-bed pyrolysis reactor
3 equipped for controlling both liquid and gaseous reagent
4 feeds. The reactor contained a preheater, a 15 inch
5 long reactor tube fabricated from 1/2 inch O.D. stain-
6 less steel tubing, a furnace in which the reactor tube
7 could be inserted, and a receiver and cold trap (accumu-
8 lator section) for collecting liquid product and water.
9 The preheater was used to preheat the helium sweep gas
10 as well as to generate steam in those examples illus-
11 trating the present invention.

12 The metal phenates in the following examples
13 were handled under an inert atmosphere of either helium
14 or nitrogen to exclude both carbon dioxide and extra-
15 neous water. All transfers were carried out under
16 nitrogen in a glove box. A small positive pressure of
17 nitrogen gas was maintained during methylation reactions
18 using a mineral oil bubbler as a pressure relief.

19 Comparative Example F.

20 1.30 g of calcium hydroxy phenate was placed
21 in the reactor tube in a glove box under nitrogen. The
22 reactor tube was connected to the preheater, capped,
23 removed from the glove box, and installed in the furnace.
24 A flow of helium sweep gas (100 ml/min.) was established
25 and the accumulator was attached to the reactor tube.
26 The preheater was heated to 250°C and the reactor tube
27 was heated to, and maintained at, 350°C for 80 minutes,
28 after which, it was cooled to room temperature under a
29 flow of helium. The accumulator section was found to be
30 empty. The reactor was capped and returned to the glove
31 box where the residue was transferred to a reaction
32 flask and methylated with 3.0 ml of iodomethane in 15 ml
33 of N,N-dimethylformamid (DMF) solvent for 30 minutes

1 at 60°C to convert phenol moieties to anisole. Gas
2 chromatographic analysis revealed that essentially all
3 of the phenol moieties (99%) remained in the residue.
4 Therefore, the calcium hydroxy phenate was thermally
5 stable at 350°C, in the absence of steam, and did not
6 release any phenols.

7 Example 19

8 The procedure of Comparative Example F above
9 was followed except the calcium hydroxy phenate was
10 contacted with steam which was generated by feeding 1.87
11 ml of water into the preheater which was maintained at
12 250°C. This amount of water represented a 12 to 1
13 molar ratio of water to calcium hydroxy phenate and was
14 fed to the preheater over a period of 10 minutes. The
15 reactor tube was maintained at a temperature of 350°C
16 during the period of steam generation as well as for an
17 additional 30 minutes to ensure complete removal of
18 volatiles from the residue. The reactor was then
19 cooled, capped, and returned to the glove box. The
20 methylation procedure of Comparative Example F was
21 carried out on the residue. No anisole was detected in
22 the product, hence, complete phenol liberation was
23 obtained by steam stripping at 350°C. Analysis of
24 the liquids in the accumulator by gas chromatography
25 indicated a quantitative recovery of phenols from
26 the calcium hydroxy phenate sample. The phenol and calcium
hydroxide were subsequently separated.

27 Example 20 and Comparative Example G

28 The procedure of Example 19 above was followed
29 except the temperature of the reactor tube was 150°C
30 for Comparative Example G and 250°C for Example 20.

1 After steam stripping the phenate sample at
2 250°C, analysis of the residue and liquid indicated
3 that 46% of the phenol moieties remained in the phenate
4 residue while 54% were recovered as phenol.

5 After steam stripping the phenate sample at
6 150°C, analysis of the residue and liquid indicated
7 that substantially all of the phenol moieties remained
8 in the residue, while only a trace (<2%) were recovered
9 as phenol.

10 The results of these two examples in combina-
11 tion with Example 19 above, in which steam stripping was
12 carried out at a temperature of 350°C, illustrate that
13 predetermined amounts of phenol can be recovered from a
14 metal phenate by steam stripping the phenate at various
15 temperatures for a given period of time and molar ratio
16 of water to phenate.

17 The data of Examples 19, 20 and Comparative
18 Example G are illustrated in Figure 1 thereof.

19 Examples 21 and 22

20 The procedure of Example 19 above was followed
21 except the molar ratio of water to calcium hydroxy
22 phenate was 4 to 1 for Example 22, and 9 to 1 for Example
23 21.

24 After steam stripping the phenate sample at
25 350°C and molar ratio of water to phenate of 9 to 1,
26 analysis of the residue and liquid indicated that
27 approximately 75 wt.% of the phenol was recovered.

28 At a molar ratio of 4 to 1, approximately
29 35 wt.% of the phenol was recovered.

1 Thus, by adjusting the molar ratio of water
2 to phenate in the steam stripping of a metal phenate at
3 a given temperature and time period, one is able to
4 recover a predetermined amount of phenol from the
5 phenate.

6 Table V below sets forth the results of the
7 above examples.

8

TABLE V

9
10

Wt.% Phenol Recovered From Calcium Hydroxy
Phenate By Steam Stripping

11	12	13	14	15	16	17
	<u>Example</u>	<u>Temp°C</u>	<u>mol ratio</u> <u>H₂O to phenate</u>	<u>Time in</u> <u>minutes</u>	<u>Wt.% phenol</u> <u>recovered</u>	
13	F	350	No H ₂ O	80	0	
14	19	350	12:1	10	100	
15	20	250	12:1	10	54	
16	G	150	12:1	10	<2	
17	21	350	9:1	10	75	
18	22	350	4:1	10	35	

19 The data of this table are also shown in
20 Figure 2 hereof.

21 Comparative Example H and I

22 The procedure of Comparative Example F above
23 was followed except for Comparative Example H, 1.30 g
24 of sodium phenate was employed; and, for Comparative
25 Example I, 1.30 g of potassium phenate was employed.
26 Analysis of the residue from both of these examples
27 indicated that no phenol was liberated and no liquid was
28 found in the accumulator.

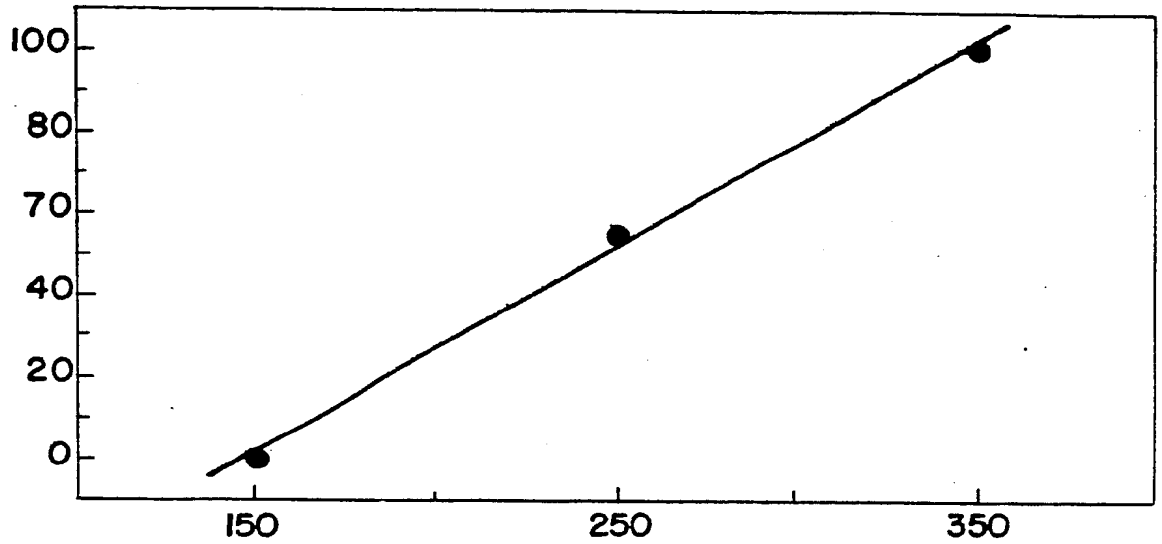
1 Examples 23 and 24

2 The experimental procedure of Example 19 above
3 was followed except that for Example 23 1.30 g of sodium
4 phenate was employed and for Example 24 1.35 g of
5 potassium phenate was employed. Analysis of the residue
6 and liquid from each example revealed that 85 wt.% of
7 phenol was recovered from sodium phenate and 86 wt.% of
8 phenol was recovered from potassium phenate.

CLAIMS:

1. A process for producing a phenol and a metal hydroxide from a metal phenate which process comprises contacting the metal phenate with steam at a temperature from about 250°C to about 450°C whereby the phenol and the hydroxide are formed and which are thereafter separated.
2. A process according to claim 1 wherein the metal of the phenate is selected from alkali metals and alkaline-earth metals.
3. A process according to either of claims 1 and 2 wherein the metal phenate is contacted with steam at a molar ratio of steam to phenate of at least about 10 to 1 and at a temperature of about 300°C to about 350°C.
4. A process according to any one of the preceding claims wherein the metal phenate is obtained by treating a phenol-containing stream containing sufficient water for metal phenate to form with a metal composition comprising one or more oxides and/or hydroxides of metals capable of forming a metal phenate with phenols of the stream, wherein the contacting is performed below the lower of the following two temperatures (i) the decomposition temperature of the resulting metal phenate, or (ii) the temperature at which detrimental thermal degradation of the stream occurs and thereafter the resulting metal phenate is separated from the stream.
5. A method according to claim 4 wherein the phenol containing stream is a waste water stream.
6. A method according to claims 4 wherein the phenol-containing stream is a hydrocarbonaceous stream.

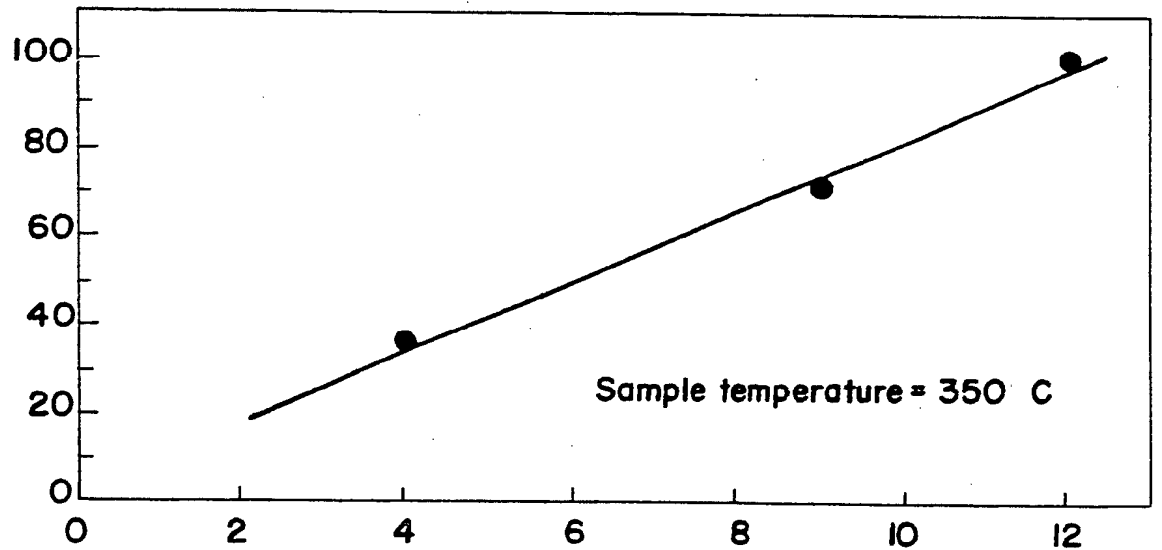
% Conversion of Calcium Hydroxy Phenate



Temperature, °C

FIG. 1

% Conversion of Calcium Hydroxy Phenate



Sample temperature = 350 C

Molar ratio of water : CPHS

FIG. 2

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31 Rec'd PCT/F... 11 JAN 2002